IMPACTS OF ENHANCED EFFICIENCY NITROGEN FERTILIZERS ON YIELD-SCALED N_2O EMISSIONS IN ILLINOIS MAIZE

BY

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THESIS

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ABSTRACT

Nitrous oxide (N_2O) is a potent greenhouse gas (GHG) with about 300 times the global warming potential of CO_2 and significant levels of this GHG come from agriculture. A two-year field experiment was conducted to assess the ability of enhanced efficiency nitrogen fertilizers (EENFs) to minimize yield-scaled N_2O emissions while maintaining nutrient utilization and crop productivity of maize. In addition to an unfertilized control (zero N), N source treatments applied at 202 kg ha^{-1} at planting included anhydrous ammonia (AA), UAN + nitrapyrin, ESN, and SuperU. Gas samples were collected using static closed chambers. Soil inorganic N concentrations, soil temperature, and precipitation were monitored throughout the growing seasons. Crop N content, grain yield, and nitrogen recovery efficiency (NRE) were also determined each year. Over the two-year trial, we found that EENFs did not consistently reduce N_2O emissions or increase grain yields relative to the conventional AA treatment. Soil N concentrations were not correlated with daily N_2O flux rates. In 2015, injected UAN + nitrapyrin increased N_2O and yield-scaled N_2O emissions relative to the other N sources, while AA produced the highest emissions in 2016, but not the highest yield-scaled emissions. These results indicate the difficulty in identifying ways to decrease yield-scaled N_2O emissions using different N sources under variable weather conditions each year that likely influenced fertilizer N transformations in soil.

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1. INTRODUCTION

To meet increasing food demand for a projected 9 billion people in 2050 with reduced environmental impacts, improvements in nitrogen (N) fertilizer use efficiency will be critical (Tilman et al., 2011). While N fertilizer inputs are important for maintaining or increasing grain crop productivity, N application also stimulates the microbial process of N_2O production in agricultural soils which is a significant environmental concern. Since the early 20th century and the development of the synthetic N producing Haber-Bosch process, concentrations of atmospheric nitrous oxide (N_2O) have increased ten-fold (Galloway et al., 2003). Approximately 75% of all N_2O emissions in the United States are a result of soil management including N fertilizer application (Davidson and Kanter, 2014). Nitrous oxide is a key greenhouse gas contributing to roughly 6% of the overall radiative forcing in the atmosphere (Ravishankara et al., 2009). Nitrous oxide has a global warming potential (GWP) 300 times that of carbon dioxide (CO_2), a long atmospheric half-life of about 120 years, and is a significant contributor to stratospheric ozone depletion (Ravishankara et al., 2009). Balancing efforts to mitigate N_2O from crop production while increasing grain yields is an important challenge for agriculture.

Illinois is a leading producer of corn (*Zea mays*) in the U.S. In 2016, average corn yield in Illinois was 12.4 Mg ha^{-1} with some 4.8 million hectares of land dedicated to its production (USDA NASS, 2016). Growers apply an average of 187.2 kg N ha^{-1} to corn in Illinois (USDA NASS, 2016) and one of the most commonly used forms of N is (injected) anhydrous ammonia. Nitrate that escapes from intensive maize production systems represents a major threat to water quality and ecosystem health. Moreover, high rates of N application have led to Illinois being a significant contributor of N_2O emissions from the Midwest (Grace et al., 2011). To reduce nutrient losses from agriculture and help combat eutrophication in natural water bodies downstream, Illinois developed the Illinois Nutrient Loss Reduction Strategy which includes comprehensive best management practices for reducing nutrient loss (Illinois EPA, 2015). While the agriculture portion of the statewide strategy is focused on reducing nitrate losses, there is no information available on N management practices designed to reduce N_2O emissions, in part due to limited data availability. To our knowledge, no published studies have assessed N_2O losses from anhydrous ammonia in corn-soybean (*Glycine max*) rotations in Illinois and evaluated whether practices aimed at increasing crop N uptake are capable of mitigation N_2O losses in these systems.

Nitrogen applied in excess of crop demand is susceptible to loss, and therefore improving crop N uptake is considered a viable strategy to reduce N losses (Feng et al., 2016). Due to the direct relationship between N_2O emissions and N application rate (Bouwman et al., 2002; Snyder et al., 2009; Park et al., 2012; Shcherbak et al., 2014), a primary focus of current N_2O mitigation strategies is reducing N rates (Millar et al., 2010). The “4R” approach to nutrient stewardship is broader – it focuses on the “right” rate, source, timing, and placement of fertilizer and is increasingly promoted as a strategy for increasing crop N use efficiency (NUE) (Snyder et al., 2009). As global NUE ranges from approximately 20% to 65% (Roberts, 2008), improvements in fertilizer management to increase NUE may represent an important opportunity to reduce environmental losses. However, current research shows that methods aimed at improving NUE do not necessarily reduce direct N_2O emissions, and more than one 4R component may be needed to see improvements (Venterea et al., 2016).

Enhanced efficiency nitrogen fertilizers (EENFs) were developed to reduce N losses and improve NUE by controlling the rate of N release or modifying the soil reactions through various modes of action which provides better synchrony between crop N demand and N availability (Hatfield and Venterea, 2014). Polymer-coated urea fertilizers are designed to release inorganic N more slowly over time as the polymer coating breaks down, potentially resulting in higher fertilizer N utilization by crops and a reduction of the quantity of available substrate for soil microbes to carry out nitrification and denitrification processes. Stabilized urea sources containing urease inhibitors slow the conversion of urea to ammonium (NH_4^+) and nitrification inhibitors slow the conversion of NH_4^+ to NO_3^-. Nitrous oxide is produced during both nitrification and denitrification steps of the N cycle and reducing available substrate for these steps should in theory reduce N_2O emissions (Baggs, 2011). Laboratory research has shown that polymer-coated urea effectively reduces N_2O emissions by about half compared to urea, likely due to slower diffusion of N through the semi-permeable polymer membrane (Awale and Chatterjee, 2017). Fisk et al. (2015) found that in a short-term incubation trial, nitrapyrin, a nitrification inhibitor, significantly decreased gross nitrification rates but its effectiveness in reducing N_2O emissions was also moderated by soil properties such as organic matter and wetting and drying of soil. The nitrification and urease inhibitors found in SuperU (N-(nbutyl) thiophosphoric triamide (NBPT) and dicyandiamide) have been shown to reduce net NO_3-N production in field and laboratory studies, both singularly and in combination (Harty et al., 2017).

Numerous studies have quantified the effects of EENFs on N_2O emissions from agricultural systems, with the majority concluding that EENFs mitigate N_2O emissions. In a global meta-analysis by Akiyama et al. (2009), nitrification inhibitors, including nitrapyrin and dicyandiamide, were shown to reduce N_2O emissions by approximately 50% across 35 different studies which included many different locations, cropping systems, soil types, and climates. Although there was greater variability in results, these authors also found polymer-coated fertilizers significantly reduced emissions compared to conventional fertilizers. Another quantitative review focused on N management in the U.S. Corn Belt determined that the combination of nitrification inhibitors NBPT and dicyandiamide proved to be the only EENF that consistently reduced N_2O emissions compared to conventional N fertilizers (Decock, 2014). Within irrigated corn systems in Colorado, Halvorson et al. (2014) found that ESN reduced N_2O emissions by 42% compared to urea, UAN with NPBT reduced N_2O emissions by 41% compared to UAN, and SuperU reduced N_2O emissions by 46% compared to urea. Halvorson et al. (2010) also found that in irrigated corn production systems in Colorado, application of SuperU resulted in significant decreases in N_2O emissions compared to urea. Fernández et al. (2015) compared N_2O emissions from urea, ESN, and anhydrous ammonia in a continuous corn system in Illinois and found that, anhydrous ammonia and urea produced 73 and 44% more N_2O emissions than ESN, respectively, across the three-year study. Omonode and Vyn (2013) demonstrated that UAN with nitrapyrin reduced N_2O emissions by as much as 44% compared to UAN alone in Indiana. However, reductions in emissions reported by Omonode and Vyn (2013) varied by location and year due to differences in soil moisture, temperature, and precipitation.

A number of field studies have also produced inconsistent results, with many experiments showing no effect or only a small effect of EENFs on N_2O emissions. In Minnesota, Venterea et al. (2011) and Maharjan et al. (2014) compared ESN and SuperU to conventional urea in corn cropping systems and found no significant reductions in N_2O emissions with these treatments. In a rainfed corn system in Iowa, Parkin and Hatfield (2014) determined that there was no difference in N_2O emissions between ESN, SuperU, broadcast UAN, and broadcast UAN with urease and nitrification inhibitors in a three-year study. Similar findings were reported for rainfed corn systems in Pennsylvania and Kentucky (Sistani et al., 2011; Dell et al., 2014), where EENFs did not consistently reduce N_2O emissions when comparing conventional fertilizers including urea and UAN to similar EENF treatments including ESN, UAN with nitrapyrin, and SuperU. Site-specific differences including soil type, climate, and management practices such as tillage and N application timing and placement may be responsible for these variable results. Moreover, with one exception (Maharjan et al., 2014), a standout difference among the studies discussed above regarding positive vs. neutral effects of EENFs was whether experiments were irrigated or rainfed, indicating that soil moisture is a primary factor influencing the ability of EENFs to reduce N_2O emissions.

Given the potential importance of EENFs as a practical management strategy that is already being promoted for reducing N_2O emissions in US Midwest corn production systems, additional research is needed to evaluate the N_2O mitigation potential of different EENFs as compared to anhydrous ammonia. In this study, we hypothesized that EENFs would decrease N_2O emissions by providing less substrate for microbial N_2O production while simultaneously increasing crop N uptake and yield. Our specific objectives were to assess soil N_2O emissions, inorganic N availability, and grain yield for three EENFs compared to anhydrous ammonia in a rainfed, corn-soybean rotation in east-central Illinois over two years.

2. MATERIALS AND METHODS

2.1 Site description and experimental design

Field experiments were conducted in 2015 and 2016 at the University of Illinois Crop Sciences Research and Education Center in Urbana, IL (40°3'60" N, 88°14'8" W). The region has a temperate climate with a 30-year (1981-2010) average temperature of 10.9°C and average cumulative rainfall of 1051 mm year^{-1}. In 2015, the predominate soil type in the field was Raub silt loam (Fine-silty, mixed, superactive, mesic Aquic Argiudolls) and in 2016 it was Drummer sily clay loam (Fine-silty, mixed, superactive, mesic Typic Endoaquolls. All slopes ranged from 0 to 2 percent. Selected soil properties for the two sites are listed in Table 1.

Table 1. Selected soil properties at the two experimental sites (0-20cm).

Soil property	2015	2016
pH	6.7	7.1
OM, %	3.6	4.3
Sand, %	9	10
Silt, %	57	58.5
Clay, %	34	31.5
Soil Textural Classification	Silty Clay Loam	Silty Clay Loam

The experiment was arranged as a randomized complete block design with four replications. Individual plots were 6.1 by 15.2 m in size, with 8 corn rows spaced 0.76 cm apart. The treatments consisted of a control (check) with no fertilizer N applied, and four N sources applied at a rate of 202 kg N ha^{-1}: injected anhydrous ammonia (AA), broadcast ESN® (polymer coated urea, Agrium Advanced Technologies), broadcast SuperU® (urea formulated with the urease and nitrification inhibitors [N-(nbutyl) thiophosphoric triamide and dicyandiamide], Agrotain International), and UAN with nitrapyrin (2-chloro-6-(trichloromethyl) pyridine), Dow Agrosciences) at 0.4 L ha^{-1}. In 2015, UAN + nitrapyrin and NH_3 were injected on 30 April. SuperU and ESN were broadcasted on 5 May. In 2016, NH_3 was injected on 22 April and UAN + nitrapyrin was injected on 23 April. SuperU and ESN were broadcast on 26 April. Each season, UAN + nitrapyrin and NH_3 were injected below the soil surface between rows approximately 6 and 14 cm deep, respectively.

For each experiment, corn was planted following soybean the previous year. Spring tillage consisted of one pass of a combination toolbar (Sunflower 6333, Beloit, Kansas) to a depth of about 9 cm prior to planting. In both years, the corn hybrid Pioneer 1221 was used. Seeds were planted at a depth of 4 cm at 34,000 seeds ha^{-1}. Planting occurred on 1 May, 2015 and 25 April, 2016. Weeds were controlled with post emergence herbicides. Both fields were tile drained.

2.2 Nitrous oxide emissions

Soil N_2O emissions were measured using non steady-state vented closed chambers adapted from Rochette and Bertrand (2008) and Venterea et al. (2016). In brief, rectangular chamber bases and lids were constructed from clear acrylic plastic, and chamber bases were installed after planting to a depth of 5 cm and remained in place for the remainder of the growing season. Chamber lids (67.3 cm length, 40.6 cm width, 19 cm height) were insulated with reflective double bubble foil insulation to minimize temperature changes during gas sampling (Ecofoil, Urbana, IA), and fitted with vent tubes and septa to serve as a sampling port for gas extraction. To create an air-tight seal during gas sampling, the bottom of lids were fitted with closed-cell foam (Lundell Manufacturing Corporation, Minneapolis, MN) and clamps were used to secure lids in place.

Measurements were performed twice per week during the period of higher anticipated N_2O emissions (May- July) and once per week thereafter until harvest (August – September). In total, 25 and 31 gas sampling events occurred in 2015 and 2016, respectively. N_2O flux measurements were generally taken between the hours of 9:00 and 11:00 am. During each sampling event, gas samples were collected at 0, 10, 20, and 30 min by extracting 20 mL of headspace air using plastic 20 mL luer-lock tip syringes with 25-guage needles. 5 mL of gas was ejected and 15 mL gas samples were immediately injected into 10 mL evacuated glass vials fitted with butyl rubber stoppers (Voigt Global Distribution Inc., Lawrence, KS) covered with clear RTV silicone adhesive sealant (Dow Corning, Midland, MI) which acted as an additional septum and prevented leakage. Gas samples were analyzed using a Shimadzu 2014 gas chromatograph equipped with an electron capture detector and auto-sampler (Shimadzu Scientific Instruments, Columbia, Maryland). Helium was used as the carrier gas. Gas standards for N_2O ranged from 0.32 ppm to 4.02ppm in 2015 and 0.1 ppm to 10.14 in 2016 (Matheson, Basking Ridge, New Jersey).

Daily flux rates were estimated from the linear increase in headspace gas concentration over time. Cumulative N_2O fluxes were calculated by linear interpolation between sampling events. The emission factor (EF) of fertilizer-induced emissions was calculated as a percentage using Eq. [1]:

$$\mathrm{EF} = \left(\frac{\mathrm{N_2O\ emissions\ of\ fertilized\ treatment} - \mathrm{N_2O\ \ emissions\ of\ unfertilized\ treatment}}{\mathrm{Nitrogen\ rate\ of\ fertilized\ treatment}}\right) \times 100 \qquad [1]$$

Yield-scaled N_2O emissions were calculated by dividing cumulative N_2O emissions by grain yield. Nitrogen recovery efficiency (NRE) was calculated as a percentage using Eq. [2]:

$$\mathrm{NRE} = \left(\frac{\mathrm{Crop\ N\ Content\ at\ R6\ of\ fertilized\ treatment} - \mathrm{Crop\ N\ Content\ at\ R6\ of\ unfertilized\ treatment}}{\mathrm{Nitrogen\ rate\ of\ fertilized\ treatment}}\right) \times 100 \qquad [2]$$

2.3 Soil and plant measurements

Surface soil samples (0-10 cm in 2015 and 0-20 cm in 2016) were collected weekly during May through July and bi-weekly from August through September. Five soil cores were collected from each plot parallel to the chamber bases within 1 m. Cores were immediately composited and placed on ice. In the laboratory, soil extractions for inorganic N analysis were performed using 2M KCl with ratio of 12 g moist soil to 100 mL KCl and 1 hr of shaking. Samples were filtered with #2 Whatman filter paper (Sigma Aldrich, St. Louis, MO). Concentrations of NO_3-N and NH_4-N were determined using a SmartChem 170 discrete wet chemistry auto-analyzer (Unity Scientific, Milford, MD). Soil moisture content for each sample was determined by oven drying soils at 105ºC for 48 hours.

Plant and grain N concentrations were determined at R6. Six plants adjacent to the harvest area were cut at ground level and separated into ear and biomass fractions. Biomass samples were shredded and dried to a constant weight at 60 ºC. Analysis of grain and biomass total N concentration was performed via combustion on an elemental analyzer by Brookside Labs (New Bremen, OH). Cob N uptake was estimated as 4.8% of total N uptake in plant and grain (McGeehan and Naylor, 1988). Grain yield was determined by hand harvesting ears shortly after R6 from 3 m of the center two rows of each plot. Grain was shelled from ears using an Almaco ECS (Nevada, IA) and yields were adjusted to 15% moisture.

Soil temperature and moisture at each experimental site were measured hourly using two Decagon Device sensors and loggers (Pullman, WA). Soil temperature was measured at two location and soil moisture was measured at eight locations, two in-row and two between-row, at two depths, 5cm and 10cm. A rain gauge (Rainwise, Trenton, ME) and data logger (Onset HOBO UA-003-64, Bourne, MA) were used to record daily precipitation for the length of the growing season. Long-term weather records at the site were obtained from the Illinois State Water Survey (ISWS, 2017).

2.4 Economic analysis

Fertilizer prices for each N source were estimated by the Illinois Fertilizer & Chemical Association based on information from commercial retailers in Central Illinois. The average corn grain price for 2015 and 2016 was based on average price data from University of Illinois Farmdoc (Farmdoc, 2017). Returns to N each year were calculated by subtracting fertilizer costs and the profit from the unfertilized control plots from the total profits for each fertilized treatment.

2.5 Statistical analysis

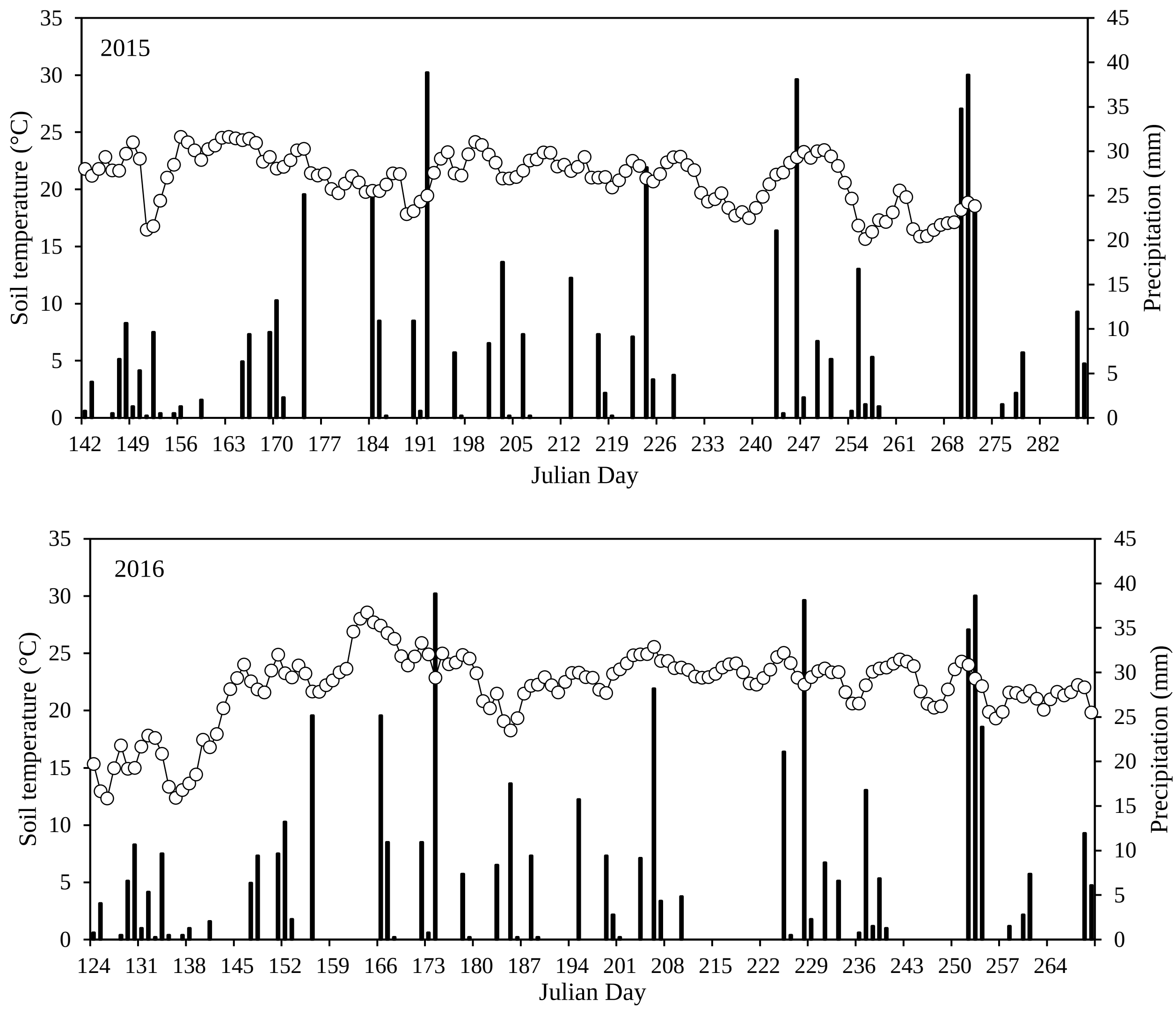
Differences in cumulative area and yield-scaled N_2O emissions, grain yield, crop N uptake, and NRE were analyzed for each year using linear mixed models (PROC MIXED) in SAS 9.4 (SAS Institute Inc., Cary, NC). Treatment was considered a fixed effect and block was considered a random effect. Least square means were compared using the PDMIX8000 macro (Saxton, 1998) at α=0.05. To meet normality assumptions, values for soil N_2O emissions and yield-scaled N_2O emissions were log transformed. Correlations between soil NO_3-N, NH_4-N, and total inorganic N versus daily N_2O flux rates were evaluated using the PROC CORR procedure in SAS 9.4.

3. RESULTS

3.1 Environmental factors

Growing season average daily soil temperature ranged from 15.6 to 24.6ºC in 2015 and 12.3 to 28.6ºC in 2016 (Fig. 1). Cumulative rainfall during the growing season was 731.5 mm in 2015 and 546.1 mm in 2016, compared to a 25-year average (1990-2015) of 515.6 mm. June 2015 had unseasonably high rainfall which resulted in it being the wettest June on record. Monthly cumulative rainfall was 276.7 mm in June 2015, compared to 121.9 mm in 2016 and the 25-year average of 114.3 mm.

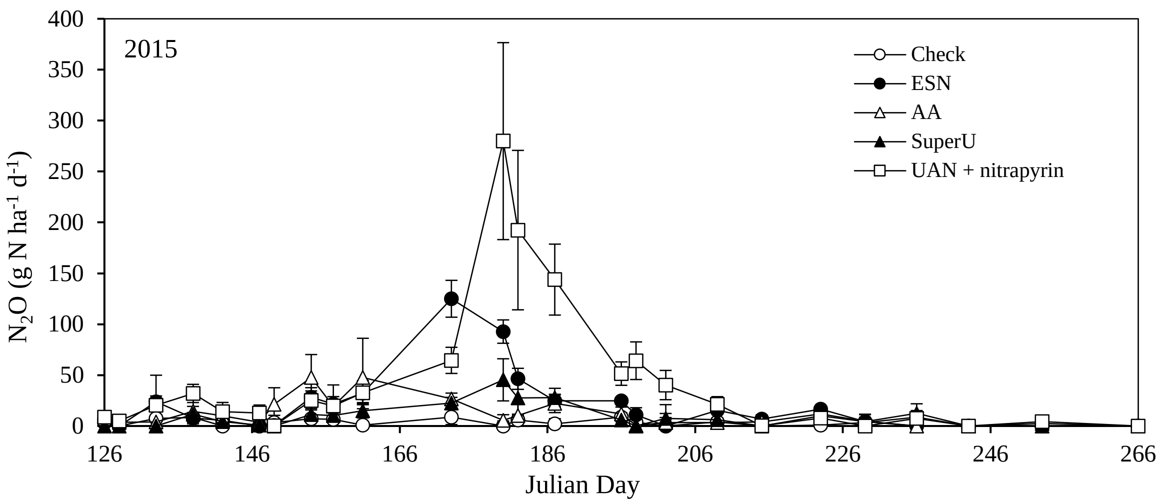
Figure 1. Daily average 10 cm depth soil temperature and precipitation for the 2015 and 2016 growing seasons (May-September).



3.2 Nitrous oxide emissions

Temporal variation in soil surface N_2O emissions followed similar patterns in 2015 and 2016. Emissions generally remained lower during the beginning and end of the growing season, with the highest emissions occurring closer to the middle of the season (Fig. 2). The period when emissions were highest in 2015 was from early June through late July, with the highest flux rate occurring on 29 June in the UAN + nitrapyrin treatment (279.9 g N_2O-N ha^{-1}). ESN was associated with higher emissions earlier in the season, resulting in the second highest high flux rate observed - 125.0 g N_2O-N ha^{-1} on 22 June. Emissions for injected NH_3 and broadcast SuperU remained relatively low throughout the growing season, with several small peaks in N_2O emissions during June. In 2016, the period of highest emissions was from early May to late June for the majority of treatments, with NH_3 injection also showing elevated emissions in April. The greatest flux rate in 2016 was observed in the AA injection treatment on 6 June (908.3 g N_2O-N ha^{-1}). The second highest flux rates were observed for ESN on the same date (220.7 g N_2O-N ha^{-}1) and also later in June (227.6 g N_2O-N ha^{-1}). In contrast to 2015, low emissions were observed for UAN + nitrapyrin throughout the 2016 growing season.

Figure 2. Daily soil surface N_2O-N fluxes in 2015 and 2016. Treatments labels refer to: unfertilized control (Check), polymer coated urea (ESN), anhydrous ammonia (AA), urea + nitrification and urease inhibitors (Super U), and UAN + nitrapyrin. Error bars indicate the standard error of four replicates Note the highest flux value for 2016 is not shown on the graph and is 908.3 g N_2O ha^{-1} d^{-1} on 6 June 2016.



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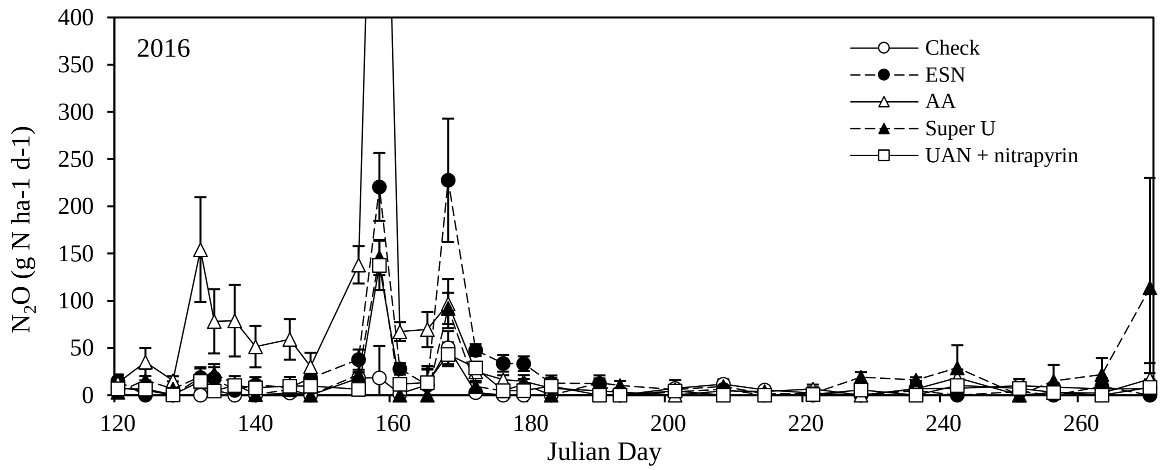


There were significant differences in cumulative N_2O emissions among treatments in both 2015 and 2016 (Table 2). In 2015, all treatments had greater cumulative N_2O emissions than the unfertilized control. Two EENF treatments, ESN and UAN + nitrapyrin, had the highest emissions, followed by SuperU and AA injection which had lower cumulative N_2O emissions. In 2016, AA injection had the highest cumulative N_2O emissions compared to the other treatments. Two EENF treatments, ESN and Super U, had lower emissions compared to AA injection, but were still greater than the control. In contrast, UAN + nitrapyrin had cumulative N_2O emissions that were not significantly different from the unfertilized control. In 2015, UAN + nitrapyrin had an EF (2.32%) that was significantly higher than the other treatments, while ESN had a significantly lower EF compared to Super U and UAN + nitrapyrin. In 2016, AA had the highest EF (2.57%), while similar emissions factors were observed for other treatments. In 2016, the EF for AA was still highest even when cumulative emissions were calculated without the extremely high N_2O daily flux rate on 6 June.

Table 2. Cumulative growing season N_2O emissions and emission factor for 2015 and 2016.

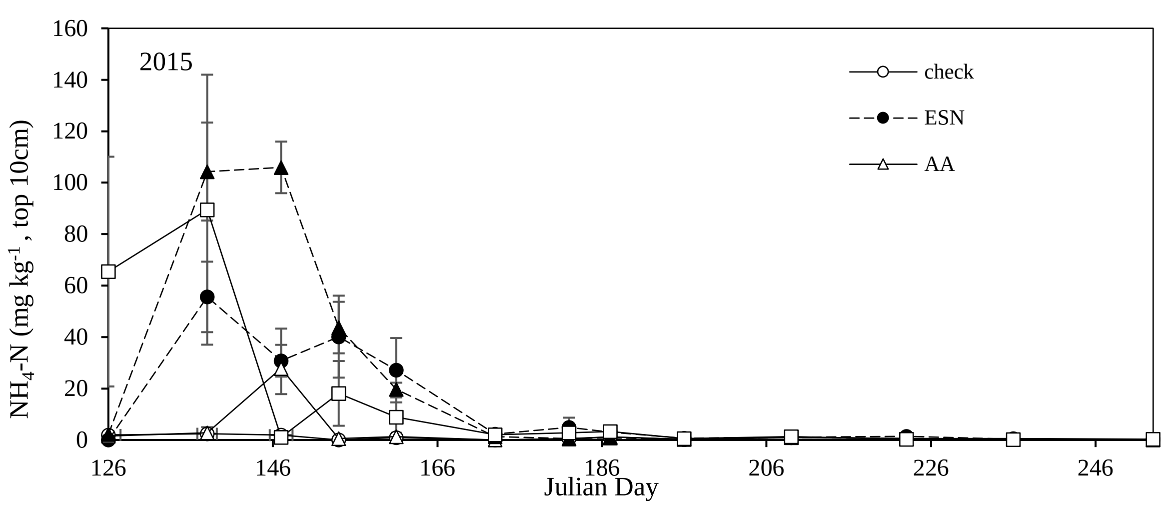
	Cumulative N_2O-N		**Emission Factor**	
Treatment	**2015**	**2016**	**2015**	**2016**
	---kg N_2O-N ha^{-1}---		----------%----------	
Check	0.72 c*	1.19 c	-	-
ESN	3.17 a	2.98 b	1.22 b	0.94 b
AA	1.55 b	6.28 a	0.59 bc	2.57 a
Super U	1.48 b	2.68 b	0.38 c	0.52 b
UAN + nitrapyrin	5.37 a	1.55 bc	2.32 a	0.28 b

* Within a column, values followed by different lowercase letter are significantly different ($P < 0.05$).

3.3 Soil N dynamics

During May in both years, there were higher concentrations of NH_4-N than NO_3-N in the surface soil sampling layers (top 10 cm in 2015 and 20 cm in 2016) (Fig. 3; Fig. 4). In 2015, Super U had the greatest and most rapid NH_4-N accumulation, providing an average of 104.3 mg kg^{-1} NH_4-N in the top 10 cm by 18 May. This was followed by UAN + nitrapyrin at 89.5 mg kg^{-1}, but by 22 June, all fertilized treatments had NH_4-N levels similar to that pf the unfertilized control. Soil NO_3-N concentrations were highest at the start of the 2015 season for UAN + nitrapyrin, and in mid-May for the other treatments, by which time soil NH_4-N concentrations had started to decline. Super U also had the highest soil NO_3-N concentrations in early May. After mid-July, all fertilized treatments exhibited soil NO_3-N concentrations similar to the unfertilized control. In 2016, AA injection resulted in the highest soil NH_4-N concentrations (20 cm sampling depth). On 3 May, there was 114.4 mg kg^{-1} NH_4-N for AA injection, followed by Super U at 60.2 mg kg^{-1} NH4-N. In late May, NH_4-N concentrations started declining rapidly, becoming similar among treatments. However, in early July slight increases in soil NH4-N were observed in early July for Super U and ESN, after which all treatments declined to concentrations similar to the unfertilized control. In 2016, the greatest soil NO_3-N concentrations occurred in June, with Super U reaching the highest concentration at 75.9 mg kg^{-1} NO_3-N in the top 20cm on 20 June. While soil NO_3-N concentrations declined across all treatments in early July, values remained slightly higher for ESN and Super U throughout much of July and August.

Figure 3. Temporal dynamics of soil NH_4-N during the 2015 and 2016 growing seasons. The depth of sampling was 10 cm in 2015 and 20 cm in 2016. Error bars indicate the standard error of four replicates.



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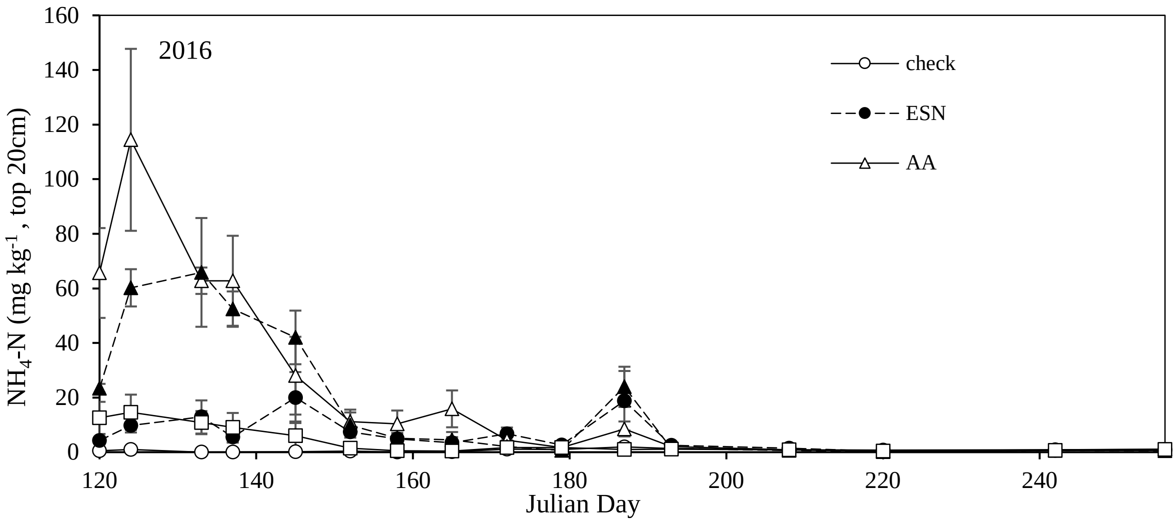
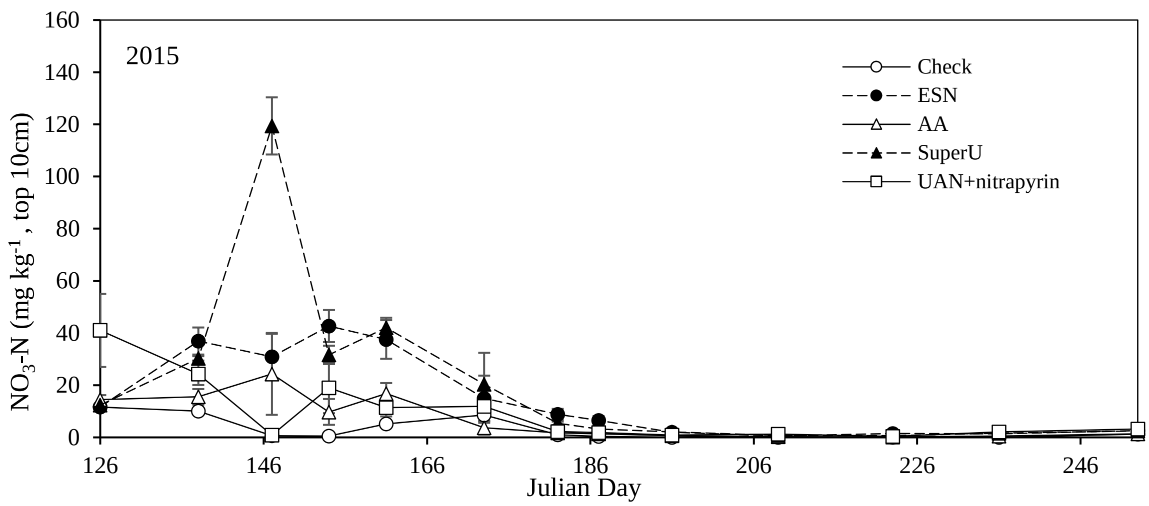


Figure 4. Temporal dynamics of soil NO_3-N during the 2015 and 2016 growing seasons. The depth of sampling was 10 cm in 2015 and 20 cm in 2016. Error bars indicate the standard error of four replicates.



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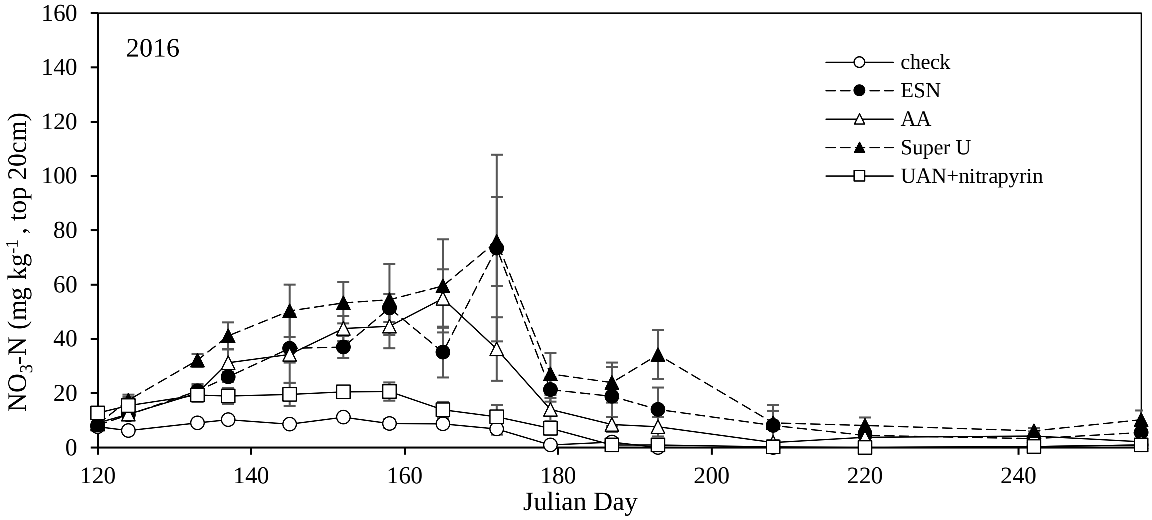

3.4 Crop response

The yield response to N fertilizer addition compared to the unfertilized control was significant in both years, with a difference of 8.5 Mg ha^{-1}, or 116% greater than the check yield in 2015, and 4.0 Mg ha^{-1}, or 39% greater than the check yield in 2016 (Table 3). In 2015, there were no yield differences between the AA and EENF treatments. In 2016, yields were similar among fertilizer treatments, with the exception of UAN + nitrapyrin, which produced a yield 20% lower than the average of the other fertilized treatments.

When cumulative N_2O emissions were divided by maize yield to determine yield-scaled emissions, trends in differences between treatments remained similar to area-scaled emissions each year. In 2015, UAN + nitrapyrin had the highest yield-scaled N_2O emissions, while yield-scaled emissions from ESN, Super U, and AA were not significantly different from that of the unfertilized control. In 2016, all treatments except AA injection had yield-scaled N_2O emissions not significantly different from the control, and the yield-scaled emissions form AA were more than double those from the other treatments. With fertilizer treatments producing similar yields, trends were generally similar between area- and yield-scaled emissions each year.

Table 3. Maize yield and yield-scaled N_2O emissions for 2015 and 2016.

Treatment	Maize Yield		Yield-Scaled Emissions	
	2015	2016	2015	2016
	--- $Mg\ ha^{-1}$---		-g N_2O-N Mg $yield^{-1}$-	
Check	7.3 b*	10.2 c	99.4 bc	118.1 b
ESN	15.7 a	15.0 a	202.2 ab	198.7 b
AA	15.3 a	15.1 a	101.9 bc	415.5 a
Super U	16.4 a	14.8 a	90.4 c	180.9 b
UAN + nitrapyrin	15.8 a	11.9 b	340.5 a	130.5 b

*Within a column, values followed by different lowercase letter are significantly different ($P < 0.05$).

Average total crop N content at R6 across all treatments, including the control, was 176.3 and 237.6 kg N ha^{-1} in 2015 and 2016, respectively. In 2015, all fertilized treatments had higher crop N content than the unfertilized control, but among fertilized treatments, only ESN was significantly higher than AA; otherwise the differences were not significant (Table 4). In 2016, the unfertilized control crop N uptake was higher than in 2015, and was not significantly different from UAN + nitrapyrin. The other three fertilized treatments had similar crop N content at R6 in 2016. Values for NRE were fairly similar among treatments in both years. In 2015, UAN + nitrapyrin had a lower NRE than ESN, whereas in 2016, AA injection had a lower NRE than both Super U and UAN + nitrapyrin.

Table 4. Total crop N uptake and nitrogen recovery efficiency (NRE) for 2015 and 2016.

Treatment	Crop N uptake		NRE	
	2015	2016	2015	2016
	--- kg ha-1---		----------%----------	
Check	83.4 c*	151.2 c	-	-
ESN	209.1 a	282.0 a	62.4 a	64.4 a
AA	189.6 b	260.8 ab	52.7 b	53.9 ab
Super U	197.5 ab	281.7 a	56.6 ab	64.7a
UAN + nitrapyrin	202.0 ab	212.4 bc	58.8 ab	30.4 b

* Within a column, values followed by different lowercase letter are significantly different ($P < 0.05$).

Average fertilizer prices reported for the treatments were: \$0.73 kg N^{-1} of AA, \$1.13 kg N^{-1} of SuperU, \$1.25 kg N^{-1} of ESN, and \$1.14 kg N^{-1} for UAN + Instinct (nitrapyrin). After fertilizer costs, the returns to N for the fertilized treatments in 2015 and 2016 were not significantly different, except for UAN + nitrapyrin in 2016. Profits were higher in 2015 than in 2016 for all fertilized treatments.

Table 5. Returns to N in 2015 and 2016 for fertilized treatments compared to the control. Corn grain prices for 2015 and 2016 were estimated at \$147 Mg^{-1} and \$139 Mg^{-1}, respectively. Values are rounded to the nearest whole dollar.

Treatment	**2015**	**2016**
	--------- \$ ha^{-1}---------	
ESN	\$980 a	\$423 a
AA	\$1030 a	\$541 a
Super U	\$1108 a	\$421 a
UAN + nitrapyrin	\$989 a	\$102 b

* Within a column, values followed by different lowercase letter are significantly different ($P < 0.05$).

4. DISCUSSION

4.1 Soil N_2O emissions

To our knowledge, this study is the first comparison of the effects of a widely used fertilizer in the US Midwest, anhydrous ammonia (AA), and three different EENFs on N_2O emissions, soil N dynamics, and yields in a rainfed corn-soybean rotation. Over two growing seasons, the EENFs we used did not consistently reduce N_2O emissions compared to AA. Much work has been dedicated to investigating the potential of EENFs to reduce N_2O emissions in recent years and other researchers have drawn similar conclusions for rainfed corn systems (Dell et al., 2014; Parkin and Hatfield, 2014). These results counter reports in other field studies and reviews that EENFs effectively reduce N_2O emissions (Omonode and Vyn, 2013; Halvorson et al., 2014; Fernández et al., 2015).

Daily nitrous oxide flux rates can be highly variable under rainfed conditions due to continuously changing soil moisture and temperature conditions. Nitrous oxide emissions are largely controlled by soil water filled pore space (WFPS) (Smith et al., 2003), as it influences many soil microbial processes including nitrification and denitrification (Bateman and Baggs, 2005). Rainfall or irrigation after a dry period generally causes a pulse of N_2O emission (Davidson, 1992; Aguilera et al., 2013) because the wetting and drying stimulates activity of nitrifying and denitrifying soil microbial communities (Mikha et al., 2005; Hu et al., 2015). In irrigated corn systems in Colorado where WFPS is more consistent, Halvorson et al. (2010a; b, 2014) showed that EENFs generally decreased N_2O emissions. In contrast, it is possible that the EENFs were inconsistent in our rainfed study because of repeated soil wetting and drying events causing microbial stimulation and peak N_2O emission events, which may have overridden any potential effects of EENFs on suppressing N_2O emissions caused by microbial activity occurring during non-peak emission events. Moreover, the unseasonably high rainfall in May through July in 2015 may have hindered the effectiveness of EENFs in this season, and it is worth investigating if with extremely high precipitation these fertilizers are largely ineffective at reducing N_2O.

The seasonal pattern of N_2O emissions observed in this study is consistent with previous research in this region (Burzaco et al., 2013; Parkin and Hatfield, 2014; Fernández et al., 2015). High emissions were generally not observed immediately following fertilizer application, but occurred later in May and June, often following precipitation events. The magnitude of background emissions from the unfertilized controls (0.72 and 1.19 N_2O-N ha^{-1} yr^{-1} in 2015 and 2016, respectively) were somewhat lower than the regional value of 1.47 kg N_2O-N ha^{-1} yr^{-1} proposed for the north-central Midwest (Millar et al., 2010). Similarly, emission factors for several treatments were below the default factor of 1% estimated for annual application of N fertilizer by the IPCC (Pachauri and IPCC, 2008). In contrast, ESN and UAN + nitrapyrin in 2015 and AA in 2016 had higher EF values. While default values are commonly used in developing GHG inventories and N_2O mitigation protocols, EFs are known to be variable (Decock, 2014; Shcherbak et al., 2014). Scherback et al. (2014) recently demonstrated the large influence of fertilizer source in addition to other experimental factors including soil carbon and pH on how EFs change in response to increasing N rate. Thus, results from this study represent an addition to the empirical evidence base for developing fertilizer-specific EFs for maize production in this region.

SuperU resulted in N_2O emissions that were among the lowest for fertilized treatments in both 2015 and 2016. Other researchers have also found SuperU to produce low amounts of N_2O compared to other fertilizer sources in their experiments (Halvorson et al., 2010a, 2014). Recent meta-analyses have shown that the combination of urease and nitrification inhibitors is a promising strategy for reducing N_2O emissions (Decock, 2014; Abalos et al., 2016). However, using Super U is not an effective N_2O mitigation strategy in all agricultural systems due to varying soil factors such as clay and organic carbon content which can potentially hinder crop N uptake from SuperU (Asgedom et al., 2014). Although ESN had similar cumulative emissions both years, relative differences between treatments changed such that ESN had among the highest emissions in 2015 and moderate emissions compared to other fertilized treatments in 2016. In comprehensive reviews of the literature, polymer coated urea has been found to be less effective at reducing N_2O emissions compared to other EENFs (Abalos et al., 2016), possibly due to the inconsistent slow release pattern of N and the effect of environmental factors on N release (Trenkel, 2010). Our results complement these broader findings and suggest that ESN may not be able to consistently reduce N_2O emissions under conditions similar to those of the present study.

The two treatments applied by injection, AA and UAN + nitrapyrin, showed results that reversed from the first to the second year. In 2015, N_2O emissions from AA were significantly lower than from UAN + nitrapyrin; in 2016, AA had significantly greater emissions than UAN + nitrapyrin. These results differ from previous research where AA injection has been found to produce more N_2O than both broadcast UAN and urea without enhanced efficiency additives (Venterea et al, 2005). Considering that addition of nitrapyrin to UAN (Omonode and Vyn, 2013; Burzaco et al., 2013) or conventional fertilizers more broadly (Akiyama et al., 2009) has been shown to reduce N_2O emissions, these findings would suggest an even greater reduction for UAN + nitrapyrin compared to AA in our experiment. These inconsistencies may be due to differences in soil moisture and temperature between the two years, as well as possible interactions with fertilizer placement. Cumulative precipitation in 2015 was 17.8 cm greater than in 2016, with higher rainfall amounts in May and June in 2015. In 2016, average daily soil temperature was greater than in 2015 (28.6ºC and 24.6ºC respectively). Additionally in 2016, there were more days when the average daily soil temperature was above 21ºC compared to 2015.

Results presented in this study are contrary to related research regarding soil N transformations for these fertilizer sources. Nitrapyrin has been shown to be more prone to degradation in warm soils (Trenkel, 2010), yet we observed that nitrapyrin was more effective in suppressing N_2O emissions compared to NH_3 injection in 2016 when soil temperatures were warmer. In contrast, soil temperatures were cooler in 2015 which would have suggested slower degradation of nitrapyrin, but UAN + nitrapyrin produced the highest N_2O emissions this year. Higher soil moisture in 2015 may have also played a role in emissions for UAN + nitrapyrin as well as AA. Anhydrous ammonia has been shown to have less retention in wet soils (Sommer and Christensen, 1992), thus high rainfall in May and June 2015 may have moved N from the AA injection deeper into the soil profile, potentially limiting upward diffusion of N_2O which is very sensitive to O_2 diffusivity (Owens et al., 2017). Given these variable results, further research on spring-applied nitrapyrin is necessary to understand the mechanisms controlling its effectiveness at reducing N_2O emissions under different temperature and soil moisture conditions.

4.2 Soil N availability

Soil inorganic N serves as the substrates for nitrification and denitrification and therefore higher concentrations of NO_3-N or NH_4-N should increase microbial reactions leading to N_2O emissions. Accordingly, available N is generally regarded as one of the most significant contributors to N_2O production (Snyder et al., 2009). Many experiments have found soil NO_3-N (Bronson et al., 1992; Thornton and Valente, 1996; Lee et al., 2006; Asgedom et al., 2014) and NH_4-N dynamics (Omonode and Vyn, 2013) are highly correlated with the N_2O emissions. However, in the present study soil NO_3-N and NH_4-N concentrations explained only a small fraction of the observed variation in daily N_2O flux rates (0.005 and -0.047 R^2 in 2015 and 0.22 and 0.42 R^2 in 2016, respectively). Our results are similar to several other authors who found NO_3-N (Adviento-Borbe et al., 2007) or NH_4-N (Barton et al., 2007; Asgedom et al., 2014) were not clearly correlated with soil N_2O emissions. The increased correlation of soil N with N_2O emissions in 2016 compared to 2015 is likely due to the greater number of samples in 2016 than in 2015. Results of the present study suggest soil N concentrations may not be a strong indicator for predicting soil N_2O emissions in response to different EENFs under conditions similar to that of this experiment.

4.3 Crop effects

Our finding that EENFs did not increase maize yield in comparison to conventional N fertilizer is in agreement with what others have reported (Halvorson et al., 2010b; a; Sistani et al., 2014; Fernández et al., 2015). We did, however, find that ESN had higher crop N uptake and NRE than AA in 2015 and both ESN and Super U had among the highest crop N uptake in 2016. However, differences in N uptake and NRE caused no major differences between treatments for grain yield in either year except for UAN + nitrapyrin in 2016. Halvorson et al. (2010b) also found that EENFs did not have any grain yield advantage over conventional fertilizers, even when some of their EENF treatments reduced N_2O emissions and increased grain N uptake. Moreover, the lack of an effect on grain yield in both 2015 and 2016 also lead to the yield-scaled N_2O emissions having the same general trends among fertilized treatments. The unfertilized control plots had significantly lower yields than the fertilized treatments in this study, which ultimately increased their yield-scaled N_2O emissions.

One possible reason for there being no positive yield response to EENFs in our experiment was the relatively high N rate applied (202 kg N ha^{-1}). It can be assumed that the N rate was non-limiting, suggesting that potential increases in soil N availability with EENFs would not have benefited yields. Sistani et al. (2014) discussed that their rate of 165 kg N ha^{-1} may have been excessive compared to crop demand, and they also showed no yield benefit of EENFs and suggested higher rainfall and better distribution to annual grain yield differences. Other studies have concluded that N rate has more of a control over grain yield than altering nitrogen fertilizer source (Halvorson et al., 2010b), which likely accounts for the similar grain yield responses to the EENFs observed here. Future studies could evaluate the effects of EENFs at lower rates to see if yields can be maintained with a reduced reliance on inorganic fertilizers (Hatfield and Venterea, 2014). In contrast to other EENFs, UAN + nitrapyrin produced significantly lower yields in 2016. Nitrapyrin has been shown reduce nitrification in soil systems by eliminating soil microbes through bactericidal action (Trenkel, 2010). While reductions in the number of nitrifying bacteria are thought to be temporary, soil microbial communities may have remained impacted later in the growing season when soil N concentrations were low and mineralization of soil organic matter and subsequent nitrification represents the dominant N source for meeting crop demand.

Reducing N_2O emissions is becoming increasingly important as it represents a major sustainability concern facing production agriculture. However, it is also argued that N_2O reductions cannot achieved be at the cost of negatively impacting yields or profits. Recent meta-analyses of field research have shown that the use of EENFs are generally not associated with yield penalties or benefits (Abalos et al., 2016; Feng et al., 2016). Although they were designed to better synchronize fertilizer N release and crop N demand, the lack of consistent yield increases suggests that the use of EENFs may represent an additional cost to farmers. In this study, after operating and fertilizer costs were subtracted from corn yield revenue, AA and EENFs had similar profits. Despite EENF costs being greater than AA (ranging from 55-71% higher per kg N), profits were generally unaffected by increased fertilizer costs associated with EENFs because they represented between 6 and 12% of total profits. As recently demonstrated by Zhang et al. (2015), future research is needed to investigate whether EENFs can be applied at reduced N rates without affecting crop yields which may reduce overall costs.

4.4 Conclusion

In this study we compared the effects of a widely used fertilizer in the US Midwest, AA, and three different EENFs on N_2O emissions, soil N dynamics, and yields in a rainfed corn-soybean rotation. Under the growing conditions observed in our two-year experiment, EENFs did not consistently reduce N_2O emissions or improve grain yield, NRE, or crop N uptake. Soil NO_3-N and NH_4-N concentrations (0.5% and 4.7% in 2015 and 21.5% and 4.2% in 2016, respectively) were not correlated with daily N_2O flux rates which suggests that soil N may not be a strong indicator for the impacts of EENFs on N_2O emissions. This highlights the fact that other soil processes controlling N_2O emissions require further investigation. Due to fertilized (202 kg N ha^{-1}) treatment yields being greater than control yields and not significantly different from each other, the yield-scaled N_2O emissions of the unfertilized control were greater than the area-scaled emissions and the trends remained relatively similar between the fertilized treatments. Even though EENFs were more costly per kg N than AA, differences between total profits were not significant because EENFs represented a small portion of total costs (6-12%). Although ESN had the highest crop N uptake and NRE in both years, it did not improve grain yields or reduce N_2O emissions compared to the other fertilized treatments, potentially due to the relatively high and likely non-limiting N rate applied in this study, or the differences in precipitation during the growing seasons. SuperU had generally low N_2O emissions in both years, which presents a possible opportunity for further research in improving the sustainability of soil fertility management strategies. Moreover, in 2015, UAN + nitrapyrin had the highest cumulative N_2O emissions (3.17 kg N_2O-N ha^{-1}) while in 2016 AA had the highest (6.28 kg N_2O-N ha^{-1}). This finding highlights the inconsistency of EENFs and the need for additional research evaluating alternative N sources under different climatic conditions and management practices to mitigate the climate change impacts of agricultural N_2O emissions.

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